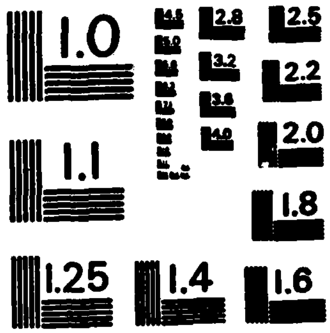
AD-A121 897 AGING STUDY OF AN ADHESIVE AND A PREPREG(U) 1/1
WESTINGHOUSE RESEARCH AND DEVELOPMENT CENTER PITTSBURGH
PA Z N SANJANA FEB 82 N00019-80-C-0596

UNCLASSIFIED F/G 11/1 NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A121897

AGING STUDY OF AN ADHESIVE

AND A PREPREG

(10)

Z. N. Sanjana
Principal Investigator

Final Report for the Period
18 Sept. 1980 to 18 Dec. 1981
Contract No. N00019-80-C-0596

February 1982

Department of the Navy
Naval Air Systems Command
Washington, D.C. 20361

Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

AGING STUDY OF AN ADHESIVE

AND A PREPREG

Z. N. Sanjana
Principal Investigator

Final Report for the Period
18 Sept. 1980 to 18 Dec. 1981
Contract No. N00019-80-C-0596

February 1982

Department of the Navy
Naval Air Systems Command
Washington, D.C. 20361

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO. AD-A122 897

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

Aging Study Of An Adhesive and A Prepreg

5. TYPE OF REPORT & PERIOD COVERED

Final Report for the period 18 Sept. 80 to 18 Dec. 1981.

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

Z. N. Sanjana

8. CONTRACT OR GRANT NUMBER(s)

N00019-80-C-0596

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, PA 15235

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

12. REPORT DATE

Feb. 1982

13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

Department of the Navy
Naval Air Systems Command
Washington, D.C. 20361

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See attached.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Block No. 20 (Abstract)

Prepregs and adhesive films which are B-stage products are used extensively in the aerospace, electrical, and communications industries. They consist of a partially reacted mixture of monomers which have been impregnated into the reinforcement. During shipping and storage, prior to use, the reactions will continue. The amount of reaction or "age" of the prepreg will depend on the conditions (temperature, humidity and time) that it has been exposed to.

This report provides data and results of studies performed on American Cyanamid's FM300 adhesive film aged under diverse conditions of temperature, time and humidity. At various times during the aging, physical properties of the adhesive were measured and the following methods were used to track the age of the adhesive: (1) dielectric analysis (DA), (2) dynamic mechanical analysis (DMA), and (3) a simple, easy to use time-temperature integrating device (TTW) which is carried with the material and provides a visual observation of the time and temperature exposure of the adhesive. It was found that DA, DMA, and the TTW can be used to follow the age of the adhesive and that they can be used as overage indicators to tell the user when the adhesive has lost its useful life. The indication by the TTW is less exact than by the other two methods.

Aging studies on Avco 5505-4 boron-epoxy prepreg were initiated. Testing is as yet incomplete and therefore the results will be presented in a future report.

FOREWORD

The following final report describes work performed on NASC Contract No. N00019-80-C-0596, "Aging Study of An Adhesive and a Prepreg". The work accomplished and reported herein was performed by Westinghouse Electric Corp., R&D Center. The program was administered by R. Dempsey for the Naval Air Systems Command.

The program was conducted in the Polymers and Plastics Department, J. D. B. Smith, Manager, with Z. N. Sanjana as principal investigator. This report covers the contract period 18 September 1980 to 18 December 1981.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

1. INTRODUCTION

The use of non-metallic materials for structural applications in high performance military aircraft is expanding. The principal non-metallics used are advanced composites and adhesives. The advanced composite material (usually graphite-epoxy) for structrual application is generally obtained from the supplier as a prepreg or a B-staged product. The adhesive is often used in a film form which consists of a B-staged product carried on a carrier cloth.

These materials consist of a partially reacted mixture of monomers which have been impregnated into the reinforcement or carrier. During shipping and storage, prior to use, the reactions will continue. The amount of reaction or "age" of the material will depend on the conditions (principally, temperature, humidity and time) that it has been exposed to. These conditions are often unknown. At a point in the age of the prepreg, some critical property or properties will deteriorate. This would then represent the end of the useful life of the prepreg.

An overage indicator should reliably inform the user of a prepreg when its useful life is over. This requires that the useful life of the prepreg be defined. With an epoxy system, this often depends on the end use for the prepreg. If the user is only interested in making flat laminates, for example, the prepreg can be used well after the point at which it becomes stiff and boardy. If, however, the use requires laying up the prepreg in a complex shape, it must be soft and tacky so that it can be draped and it can adhere to itself. In general, the end point of the useful life of a prepreg occurs when some critical property begins to be adversely affected. The critical property concerned will depend upon the end use intended for the product. Similar considerations apply to adhesives.

The overage indicator then may be either the critical property itself or some other measurement which correlates well with the loss of the critical property. The latter affords more flexibility and generality of application since, as observed above, the critical property could change depending on the material and the end use.

It is particularly necessary to know the age of the material if it is to be used under field conditions (such as at a remote base or on an aircraft carrier) to effect repairs to a composite structure. In such situations, the prepreg or adhesive is used infrequently and long periods of storage are possible. Exhaustive testing of the material prior to use is not feasible and an overage indicator would be most useful. A simple overage indicator would obviously have the greatest advantage for field use whereas a more complex, rigorous test would be more appropriate for in-plant use.

This report concludes the aging studies carried out on FM300 adhesive. In a previous report[1], data on aging of FM300 under three different conditions was presented. This report presents data on aging the adhesive under three additional conditions and on two batches of adhesive. Several methods are described which successfully track the age of the adhesive and which can be used as overage indicators. These are dielectric analysis (DA), dynamic mechanical analysis (DMA), and a time-temperature integrating indicator (TTW). The latter is a simple device which is carried with the prepreg and should be most useful for field use. The other two methods, while simple to use, require analytical equipment. The TTW is no longer being manufactured; therefore, an alternative should be evaluated.

The present work reported in this document is a continuation of effort reported earlier[1-3] and therefore should be read in conjunction with these reports.

2. SUMMARY

The method used in this study was to determine (for a given material) that critical property which is the first to deteriorate when the material is aged in shipping, storage, and handling. Various techniques are then used to track the aging of the prepreg under diverse storage conditions. The results obtained are correlated to the deterioration in the critical property. Thus each technique provides a number (or value) which is then used as a decision point to reject that lot of material as having exhausted its useful life.

Under the present contract the material examined is FM300 adhesive supplied by American Cyanamid Corp., Havre de Grace, Maryland. For the adhesive the critical property should be determined by the supplier and user but our tests indicate that adhesive flow is the first property to deteriorate with aging of the unreacted adhesive film. The first mechanical property to deteriorate is climbing drum peel strength, and we used it as the critical property.

Adhesive

Aging studies on adhesives were initiated during the last period and were completed in this reporting period. An epoxy film adhesive - FM300 from American Cyanamid - was selected for study. The uncured epoxy film adhesive as-received was aged at the following conditions:

a. 100°F 10% RH

b. 100°F 80% RH

c. Laboratory ambient (72°F 35% RH average conditions).

Results for the above conditions were reported earlier.[1] In this report data on aging of the film adhesive under the following conditions is presented:

d. 120°F 20% RH

e. 120°F 80% RH

f. 140°F 80% RH

During the aging of the adhesive under the above conditions, the following tests were performed:

Tests of Age Indicators

- Time Temperature Integrator (TTW): Several types of indicators called Time-Temperature Watch were obtained and exposed to the same aging conditions as the adhesive. The purpose was to see if under diverse aging conditions, the devices would track the age of the adhesive and would provide a value which would correlate with the loss of the critical property.

- Dielectric Analysis (DA): During the aging, at periodic intervals, measurements were made on the adhesive using an automatic dielectrometer. The measurements were made under dynamic temperature conditions to obtain the temperature of the relaxation peak in dissipation factor.

- Dynamic Mechanical Analysis (DMA): At periodic intervals during the aging, the temperature of the relative damping peak was obtained using a dynamic mechanical analyzer (DuPont Model 980).

Tests of Adhesive Performance

At periodic intervals during the aging of the adhesive, the following properties were measured:

- Flow at 40 psi on predried samples.

- Lap shear strength of aluminum-to-aluminum joints. Three conditions were used to test the joints: (1) @ 250°F, (2) @ 250°F after 24 hrs at 250°F, and (3) @ 200°F after 24 hrs water boil.

- Peel strength of the tool-side face of bonded honeycomb panels using a climbing drum test procedure.

Results of the tests on indicators and on adhesive performance were correlated to determine the critical property of the adhesive and to determine if the overage indicators would provide a single value for the end of the useful life of the adhesive under diverse aging conditions.

3. EXPERIMENTAL

3.1 MATERIALS

FM300 adhesive manufactured by the Bloomingdale Division of American Cyanamid Corp. was selected to determine if the various overage indicators developed for prepreg could also be used with adhesives. The selection of this adhesive for study was based on its extensive use in naval aircraft. All of the work reported here was performed on one batch of FM300 adhesive film of nominal weight 0.10 lbs/ft^2 which was ordered to meet McDonnell Douglas Specification MMS350 Type 1. The batch number was B-360. During the investigation, another batch of material (B-377) was ordered. Our tests showed this material to be much more advanced than the material from B-360. The supplier was contacted about the high state of advancement of the material received from batch B-377 and their records show that the roll received by us was impregnated at the end of the batch and that this would result in a higher state of advancement, even though it met specifications. It was decided to age both lots of material for the aging studies performed at 120°F, 80% RH and 140°F, 80% RH. This was done to observe the effect on aging characteristics of lot-to-lot variations. Within this report the lots are identified by their batch numbers.

3.2 OVERAGE INDICATORS

3.2.1 <u>Time-Temperature Integrators (TTW)</u>

These integrators are devices that integrate the time and temperature to which they have been exposed and display the integrated product as a color change on a numbered strip. The change in color may then be correlated to the end of the useful life of the prepreg or adhesive, or, in general, to any material that ages during shipping and storage.

One type of integrator was investigated in the course of this study. It is called Time-Temperature Watch (TTW) and is supplied by the Info-Chem Division of Akzona, Inc. The supplier is no longer marketing

this device but since many of the tests were completed, it was decided to report the data. Another time-temperature integrator manufactured by Allied Corporation is being evaluated for this application as a substitute for the TTW. Results of this evaluation will be presented in the next report.

In the previous reports[2,3], it was concluded that a Type 33 TTW was appropriate for use as an overage indicator for 3501-6/AS prepreg. Type 30, 33 and 39 TTWs were evaluated during the aging studies on FM300 adhesive.

3.2.2 Dielectric Analysis (DA)

An automatic dielectrometer (Tetrahedron, Audrey II, Model 203) was used to monitor the aging of adhesive film and to define an overage condition for the materials. The procedure and techniques used were described in detail in References 2 and 4. In brief, measurements are made in the temperature variant mode at a rate of 10°C/min and 1 kHz frequency. The sample used consists of 1 ply of adhesive film (dried in a desiccator for at least two hrs) under 1 ply of 1 mil thick polyimide film and the temperature of the first peak in dissipation factor is measured. This peak increases with age of the material.

3.2.3 Dynamic Mechanical Analysis (DMA)

A DuPont Instruments, 980 Dynamic Mechanical Analyzer was used to measure the change in prepreg age as described in detail in References 2 and 5. If brief, a 1" x 1/2" sample of prepreg is cut, dried in a desiccator for a minimum of two hrs and then placed in the clamps of the DMA. The DMA is then cooled to -20°C after which it is heated at a programmed rate of 5°C/min. As the prepreg heats up it undergoes a transition which results in a peak in the relative damping curve. The temperature of this peak was successfully used to characterize the age of the prepreg. As the prepreg ages, the temperature of the peak in relative damping increases.

3.3 ADHESIVE PERFORMANCE

Due to the limited scope of this program it was decided to limit tests of adhesive performance to key tests which are most likely to be affected by adhesive age. It is generally believed that the principal effect of environmental aging on the uncured adhesive film is to reduce its flow. Thus, bonding performance that is most affected by adhesive flow should suffer the earliest degradation due to aging of the uncured adhesive film.

Therefore, the following performance tests were decided upon in consultation with NAVAIR and are described here.

3.3.1 Adhesive Flow

(a) Six 1.5" diameter discs of the adhesive were stamped out with a die.

(b) The area of the six discs were measured using a compensating polar planimeter.

(c) The release liner was removed and the six discs were placed in a vacuum desiccator containing dry desiccant for between two to three hrs.

(d) The discs were removed from desiccator, the paper support was removed and they were placed at least 4" apart between two sheets of Mylar. The sandwich was placed between stainless steel plates and in an autoclave.

(e) Autoclave pressure was adjusted so that a true pressure of 40 ± 2 psi was applied to the disc. The autoclave was heated at about 5°F/min to 350 ± 5°F and held at temperature and pressure for 60 mins.

(f) The autoclave was then cooled to under 150°F while maintaining the pressure; after venting the discs sandwiched between the Mylar sheets were removed from the autoclave.

(g) Area of each specimen was measured using a compensating polar planimeter.

(h) The percent flow was calculated as

$$\% \text{ Flow} = \frac{\text{Final Area} - \text{Original Area}}{\text{Original Area}} \times 100 \ .$$

3.3.2 Lap Shear Strength of Aluminum-to-Aluminum Joints

At periodic intervals during adhesive aging, samples of the adhesive were removed from the aging environment and were used to form lap shear joints with 7075-T6 bare aluminum alloy.

The aluminum surface was prepared for bonding as follows: The panels were vapor degreased and then immersed in alkaline cleaner at a temperature of 150 ± 5°F for 15 mins. The panels were then immediately rinsed in tap water and deionized water. They were then etched in a sodium dichromate/sulfuric acid solution maintained at 155 ± 5°F for 15 mins. On removal from the acid bath the panels were immediately rinsed in tap water and deionized water at which point the panels were checked for water-breaks and those not free of water-breaks were reprocessed. The panels were then dried in an air-circulating oven at 140°F. This procedure is in general accord with ASTM D2651-79, "Standard Practice for Preparation of Metal Surfaces for Adhesive Bonding".

Within two hours of drying the panels were primed using BR127 primer. The primer was kept in a freezer at 0°F and was not aged in any way. Prior to use the primer was allowed to warm to room temperature on a roller mixer. This allowed thorough mixing and suspension of the primer and vehicle. The primer was sprayed on to the panels using an air sprayer to provide a cured thickness of about 0.0002". The primer was allowed to air dry for 30 mins and was then cured for 45 ± 10 mins at 250°F. The primed panels were allowed to cool, stacked with kraft paper between each panel and were then packed in sealed polyethylene bags until needed for bonding.

Plates 9" long by 4" wide were bonded together to form standard lap shear strength specimens - 7" long with a 1/2" bonded overlap. The 9" plate yielded seven 1" wide standard specimens and the edges were discarded. The adhesive was applied to the area to be bonded and the joint was press cured at a pressure of 50 psi. The joint was heated to 350° $\pm$ 5°F at about 5°F/min and allowed to cure for 75 + 15 mins. Pressure was maintained during cool down to room temperature. It was decided to use a press instead of an autoclave so as to allow the joint to form without any bondline control. Then the adhesive as it aged would flow less, form a thicker bondline and therefore form weaker bonds.

After being cut into 1" wide specimens the joints were tested in accordance with ASTM D1002 to obtain the lap shear strength. Five replicates were used per test. Three conditions were used to test the bonds formed by the adhesive: (1) @ 250°F, (2) @ 250°F after 24 hrs at 250°F, and (3) @ 200°F after 24 hrs water boil.

3.3.3 Climbing Drum Peel Strength

The peel strength of adhesively bonded facing skins to the core is affected by adhesive flow because a large part of the bond strength of the panel is due to the adhesive flowing into the core and up the sides of the core ribbons to form a fillet. As the adhesive ages its molecular weight increases and its viscosity at any temperature increases, therefore its ability to flow into the honeycomb core and form the bond is reduced. This is particularly noticed on the lower face (or tool face) of the panel because at that face the adhesive has to flow up the core ribbon surface utilizing surface tension forces, without the assistance of gravity.[1]

The peel strength of the adhesive was obtained during the aging of the adhesive film by periodically removing the adhesive from the aging environment and using it to bond honeycomb panels.

Facing skins were cut from 2024-T3 bare aluminum and were cleaned, acid etched and primed as discussed in Section 3.3.2. The

core was cut from 0.625" thick, 3/16" cell size honeycomb of 0.002" foil thickness 5056-H39 aluminum. Panels were molded in 12" by 10" size to yield three specimens 12" by 3". The core ribbon direction and film carrier warp direction were kept parallel to the 12" dimension and the adhesive was so placed that the polyethylene liner side was kept against the core.

The panels were bonded in a press at 50 psi pressure. The cure temperature of 350° $\pm$ 5°F was reached at a rate of about 5°F per minute and was held for 75 + 15 mins. After cooling under pressure the specimens were cut and tested for the climbing drum peel strength at room temperature according to ASTM D1781-76. The strength is reported in in.-lbs/in. width for an average and standard deviation of six samples per test.

4. RESULTS AND DISCUSSION

Data from the aging studies is presented in graphical form in Figures 1-12. Error bars on the data points represent $\pm$ 1 standard deviation. Data for the TTW does not have error bars because the readings were usually within one-half unit of each other and the reading accuracy is about the same in the present package configuration.

4.1 120°F, 20% RH AGING

This aging experiment was conducted on material from batch B-360 only and the results are shown in Figures 1-4. Figure 1 presents the TTW and flow data as a function of adhesive age at 120°F and 20% RH. As expected the flow diminishes with adhesive age and this results in a reduction in the climbing drum peel strength after about eight days as shown in Figure 2. Also shown in Figure 2 is the temperature of the peak in damping as obtained by DMA. The data shows low scatter and a good correlation of the temperature increasing with aging of the adhesive film. The DA data of Figure 3 also shows the same trend with aging of the adhesive. At both observed frequencies, the temperature of the first

peak in dissipation factor increases with age. The lap shear strength data of Figure 4 shows the same behavior upon aging of the adhesive as data reported previously[1] for other aging conditions. Upon aging there is an increase in shear strength up to about eight days, thereafter the strength diminishes. But, even after 20 days aging, when there is essentially no flow (Figure 1) the lap shear strength values are above the values obtained for unaged material.

4.2 120°F, 80% RH AGING

During this aging study both lots of material obtained, as described in Section 3.1, were aged to study differences in aging characteristics.

The results for this aging condition are shown in Figures 5-8 for both lots of adhesive. Figure 5 presents the flow and TTW data. The flow data (lower half of Figure 1) clearly demonstrates the difference between the two lots. B-377 had an initial flow of only 140% where B-360 was around 450% in flow. Figure 6 presents the climbing drum peel strength data in the upper half and the DMA damping peak temperature in the lower half. It is interesting to note the differences in climbing drum peel strength between the two lots. B-377 initially had the same peel strength as B-360 - about 35 in. lb/in. But on aging the adhesive at 120°F and 80% RH the peel strength of the lot B-377 declined rapidly and was almost zero in four days. Whereas B-360 maintains a 35 in. lbs/in. for at least six days before declining rapidly.

The flow and peel strength data indicate that B-377 is much more advanced than B-360 at the beginning of the test series. The DMA data (lower half of Figure 6) and DA data (Figure 7) support the conclusion that lot B-377 is more advanced (higher Tg) than B-360. The rate of advancement during the aging is similar for both. The DA and DMA data for B-377 do not reflect the rapid deterioration in peel strength or flow This seems to indicate that the lot-to-lot differences cannot be simply explained by advancement differences. Without doing a complete preparative

liquid chromatography and fourier transform infrared analysis of the adhesive lots to determine chemical identity, we cannot explain the divergence.

Figure 8 presents the lap shear strength data which shows that while initially both lots have similar values, upon aging B-377 deteriorates somewhat more rapidly.

4.3 140°F, 80% RH AGING

The results for this aging condition are shown in Figures 9-12 for both lots of adhesive. The flow data in the upper half of Figure 9 shows the large difference between the two lots of adhesive in initial flow - 480% and 140%. Again, it should be emphasized here that the differences noted by us are not necessarily batch-to-batch differences. The roll received by us could well have been different from other rolls cut from the same batch (B-377) and information provided by the supplier (see Section 3.1) would indicate that.

The differences between the two lots of material are also clearly shown by the climbing drum peel strength data shown in Figure 10, top half. The peel strength of the material from batch B-360 is maintained at about 35 in. lb/in. for two days before rapidly declining. Whereas for B-377 the peel strength declines rapidly upon exposure of the adhesive to the aging environment of 140°F, 80% RH and in two days the peel strength is <5 in. lb/in. These differences are similar to the differences shown for 120°F, 80% RH aging condition in Figure 6.

DMA and DA results presented in Figures 10 and 11 show the usual pattern of increasing temperature at the peak that has been found in the past with the FM300 adhesive and the 3501-6/AS prepreg. The DMA and DA data show that the material from batch B-377 is more advanced than the material from B-360. However the differences in the DMA and DA data between the two lots are not as dramatic as reflected in the flow and climbing drum peel strength data. As discussed in Section 4.2, this is somewhat puzzling and would indicate that differences in the two lots of adhesive cannot be attributed purely to differences in advancement.

Figure 12 presents the lap shear strength data of aluminum-to-aluminum joints for adhesive film aged at 140°F, 80% RH. The data shows a decline in shear strength after three days aging of the adhesive film. The differences between the two lots are noticeable with B-377 producing lower lap shear strengths in general.

4.4 SUMMARY OF FM300 AGING

Table 1 summarizes the data for various aging conditions for FM300 film adhesive. The data of material from batch B-377 is excluded from the summary table because of its vastly different behavior. The first row presents the time taken for the peel strength to drop below 30 in. lb/in. This value is arbitrarily chosen to permit comparisons with values of the overage indicators. The time it takes at various aging conditions for the peel strength to drop below 30 in. lb/in. is plotted in Figure 13 as an Arrhenius plot. While the data is limited, the points fit a reasonable linear plot with an activation energy of about 13.5 kcals/mol - typical of most epoxy polymerization reactions.[6] The acceleration of degradation caused by high humidity is noted by the shift to lesser times for the 80% RH aged adhesive. The flow data of Table 1 can be similarly treated and will result in an Arrhenius plot of comparable activation energy except that scatter in the data is greater.

The summary data in Table 1 can be used to define an overage condition by the three methods chosen by us. Using dynamic mechanical analysis (DMA), when the temperature of the peak in relative damping is 32°C or greater, the adhesive has reached the end of its useful life. We are assuming that when the climbing drum peel strength drops below 30 in. lb/in. the useful life of the adhesive is over. (Any other criteria for end-of-life may also be selected and correlated to the overage indicators.) Using dielectric analysis (DA), when the temperature of the peak in dissipation factor reaches 94°C or higher the adhesive has reached the end of its useful life. Using the time-temperature watch (TTW), the end of useful life of FM300 occurs when the Type 33 TTW shows a reading of 9 or greater. These values for the overage indicators

were selected to be conservative, i.e., the lowest value obtained under any aging condition was selected.

TABLE 1 - SUMMARY OF SELECTED DATA ON AGING OF FM300 ADHESIVE FILM

	Aging Condition					
	Ambient* 72°F	100°F* 10% RH	100°F* 80% RH	120°F 20% RH	120°F 80% RH	140°F 80% RH
Peel Strength <30 in. lb/in. (days)	64	17	12	10	7	25
Flow <300% (days)	22	4	4	6	3	1
DMA when peel strength <30 in. lb/in. (°C)	35	32	32	38	38	35
DA at 1.0 kHz when peel strength <30 in. lb/in. (°C)	94	95	94	99	98	95
TTW Type 33 when peel strength <30 in. lb/in. (units)	>10	>10	10	>10	10	9

*NOTE: Data in first three columns are from Reference 1.

5. AGING OF AVCO 5505-4 BORON-EPOXY PREPREG

The purpose of this study was to determine the storage stability of this boron reinforced material. If production of the prepreg ceases, then for repair purposes, large amounts of the prepreg will have to be stored under freezer (0°F) conditions. Thus it was deemed necessary to initiate an aging study to determine (a) the out time of the prepreg under RT and above RT conditions, and (b) the storage stability at 0°F. Recognizing that testing prepreg aged at 0°F may take several years, it was decided to accelerate the process somewhat by aging the prepreg at temperatures above 0°F but not above the Tg of the prepreg. This because above its Tg, the prepreg would be in a rubber phase and reaction rates would be accelerated compared to the glass phase below the Tg.

Therefore reaction data obtained in the rubber phase cannot necessarily be extrapolated to reaction in the glass phase.

To define the out time of the prepreg at RT and above and the effect of humidity, it was first decided to age the prepreg under the following three conditions: (a) laboratory ambient, (b) 120°F, 10% RH, and (c) 120°F, 90% RH. To determine the storage stability of the prepreg, aging will be carried out at 50°F, 40°F and 20°F. Some prepreg was obtained Dec. 1980 and stored at 0°F and will be used to provide spot checks.

At the end of this report period, aging study on Avco 5505-4 at laboratory ambient (average conditions 72°F, 35% RH) has been completed but all test data are not available. The data will be presented in a future report report, where it will be consolidated with the other aging studies on the same materials.

6. CONCLUSIONS

1. Dielectric analysis measurements can be used to follow the aging of uncured FM300 adhesive and to indicate when the useful life of the product may be over.

2. Dynamic mechanical analysis measurements can be used to follow the aging of uncured FM300 adhesive and to indicate when its useful life is over.

3. The TTW type 33 is a fair indicator of an overage condition for FM300 adhesive.

4. Aging the uncured adhesive at ambient and superambient conditions causes a rapid change in the flow of the adhesive but this does not readily translate into a deterioration of tested mechanical properties.

5. Climbing drum peel strength was the first mechanical property to deteriorate due to aging of the uncured film.

6. Lap shear strength of aluminum-to-aluminum bonded joints do not appear to be sensitive to aging of uncured adhesive film within the limits evaluated.

7. REFERENCES

1. Sanjana, Z. N., "Overage Indicators For Prepregs and Adhesives", Final Report for the Period 4 Aug. 79 to 3 June 1980, Contract No. N00019-79-C-0500, July 1980.

2. Sanjana, Z. N., "Overage Indicator for Graphite Fibeı Epoxy", Final Report for the Period 15 June 77 to 14 June 1978, Contract No. N00019-77-C-0247, June 1978.

3. Sanjana, Z. N., "Overage Indicator for Graphite Fiber Epoxy Prepreg", Final Report for the Period 5 Jan. 79 to 5 Sept. 79, Contract No. N00019-78-C-0600, Sept. 1979.

4. Sanjana, Z. N., "The Use of Dielectric Analysis in Characterizing the Degree of B-Staging and Cure of Composites", Sci. and Tech. of Polymer Proc., edited by Nam P. Suh, MIT Press (1979), pg. 827.

5. Sanjana, Z. N., "Overage Indicators for Prepreg Products", SAMPE Jnl., V. 16, Pg. 5 (1980).

6. Dutta, A and Ryan, M. E., "Effect of Fillers on the Kinetics of Epoxy Cure", J. Appl. Polym. Sci., V. 24, Pg. 635 (1979).

Z. N. Sanjana
Polymers & Plastics Department

Approved

J. D. B. Smith, Manager
Polymers & Plastics Department

Curve 727645-B

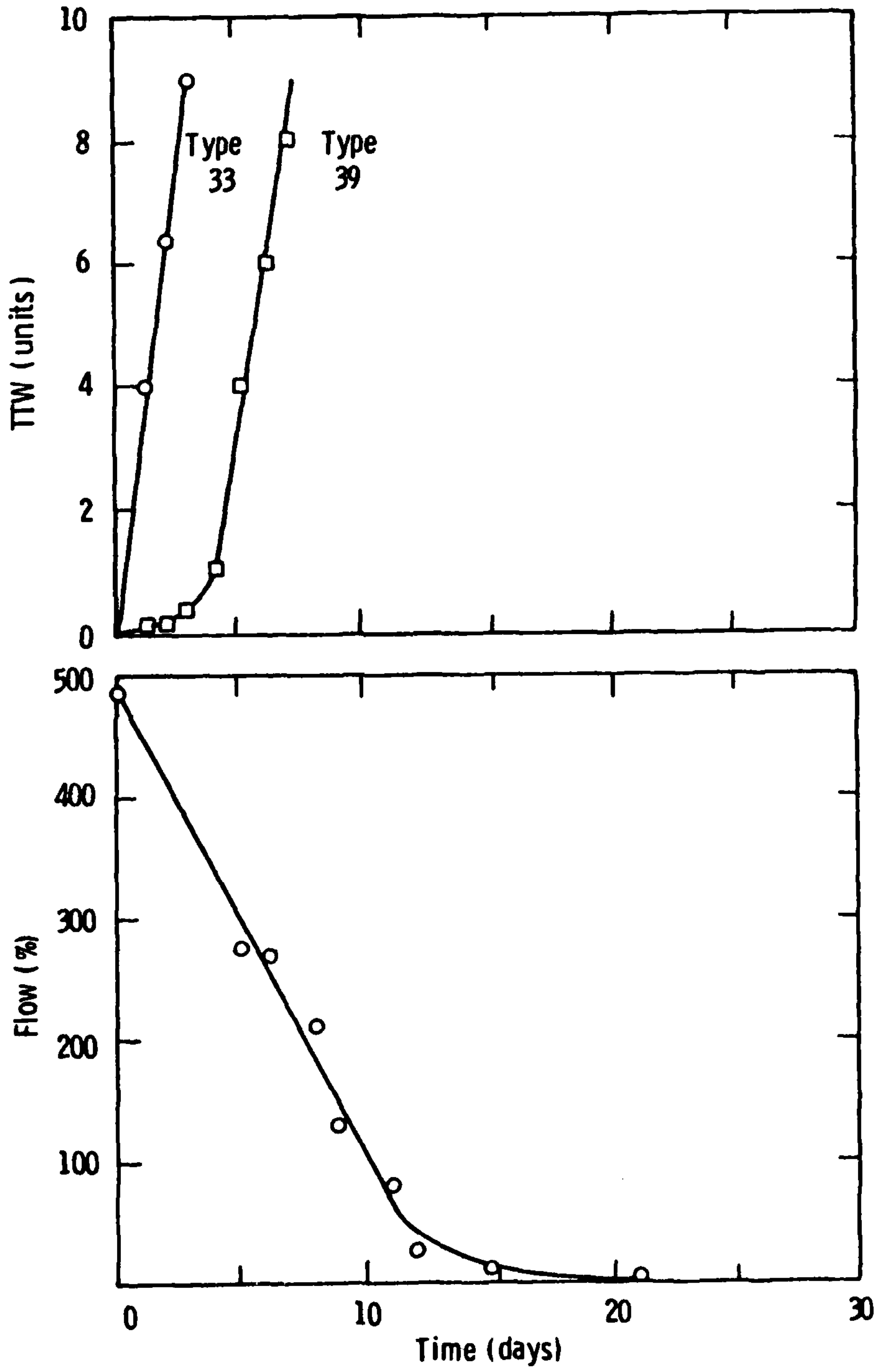


Fig. 1 — Aging at 120°F and 20% R.H. Flow and TTW data for FM 300 adhesive (Lot B-360)

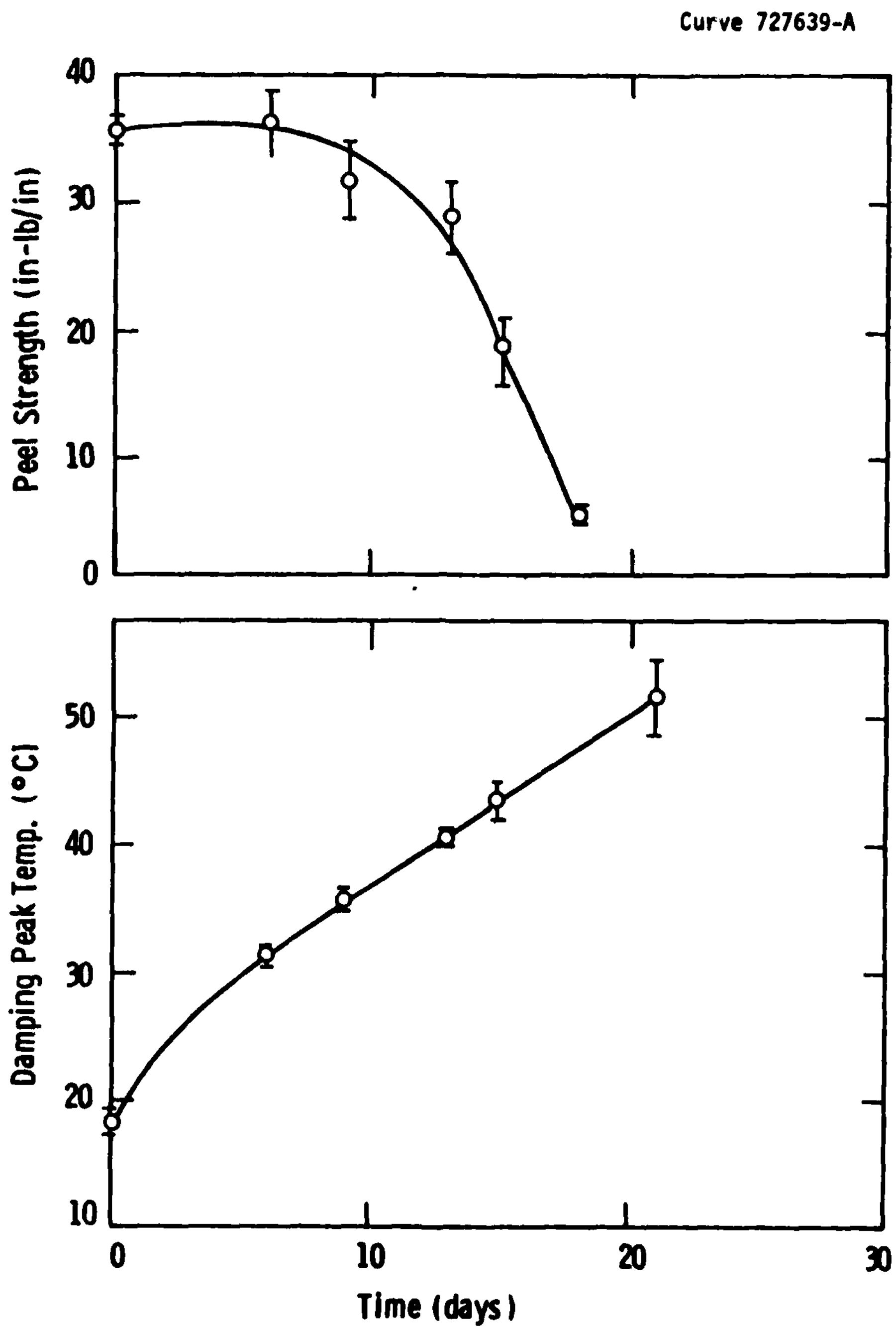


Fig. 2 — Aging at 120°F and 20% R.H. Climbing drum peel strength and DMA data for FM 300 adhesive (Lot B-360)

Curve 727640-A

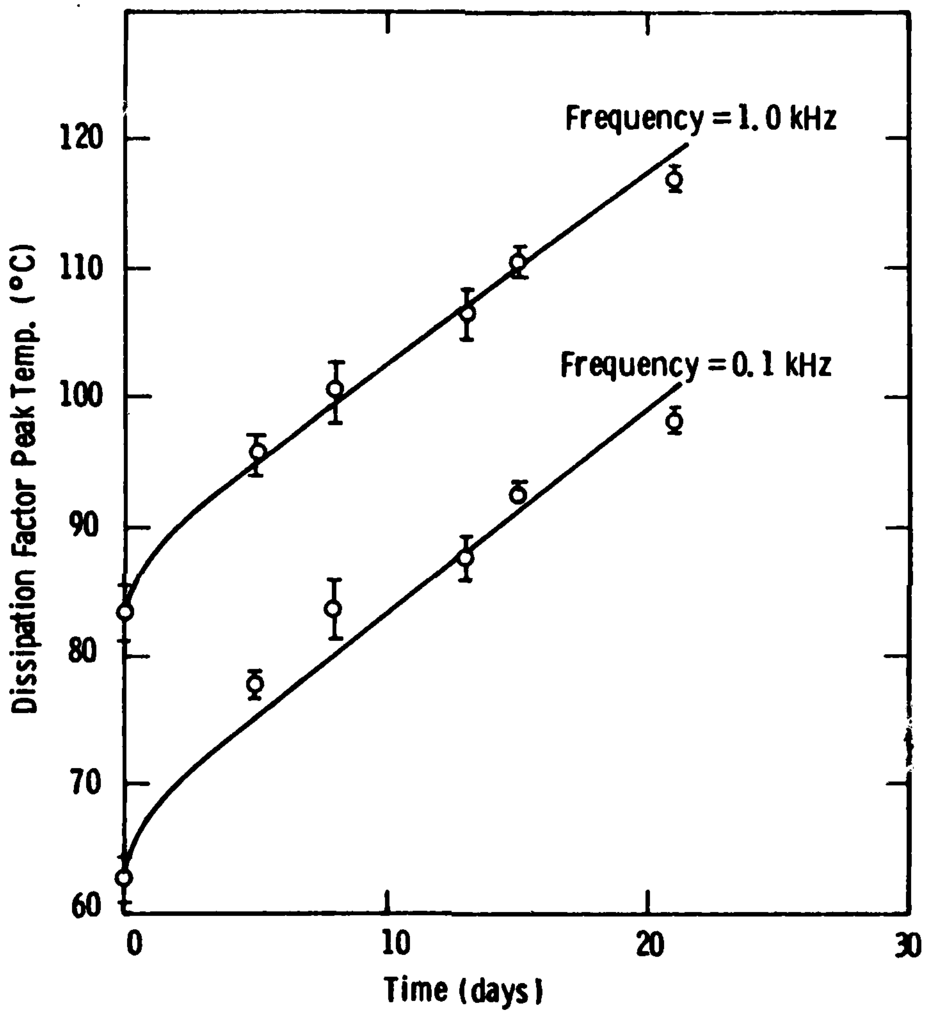


Fig. 3 — Aging at 120°F and 20% R.H. Dielectric analysis data for FM 300 adhesive (Lot B-360)

Curve 727643-B

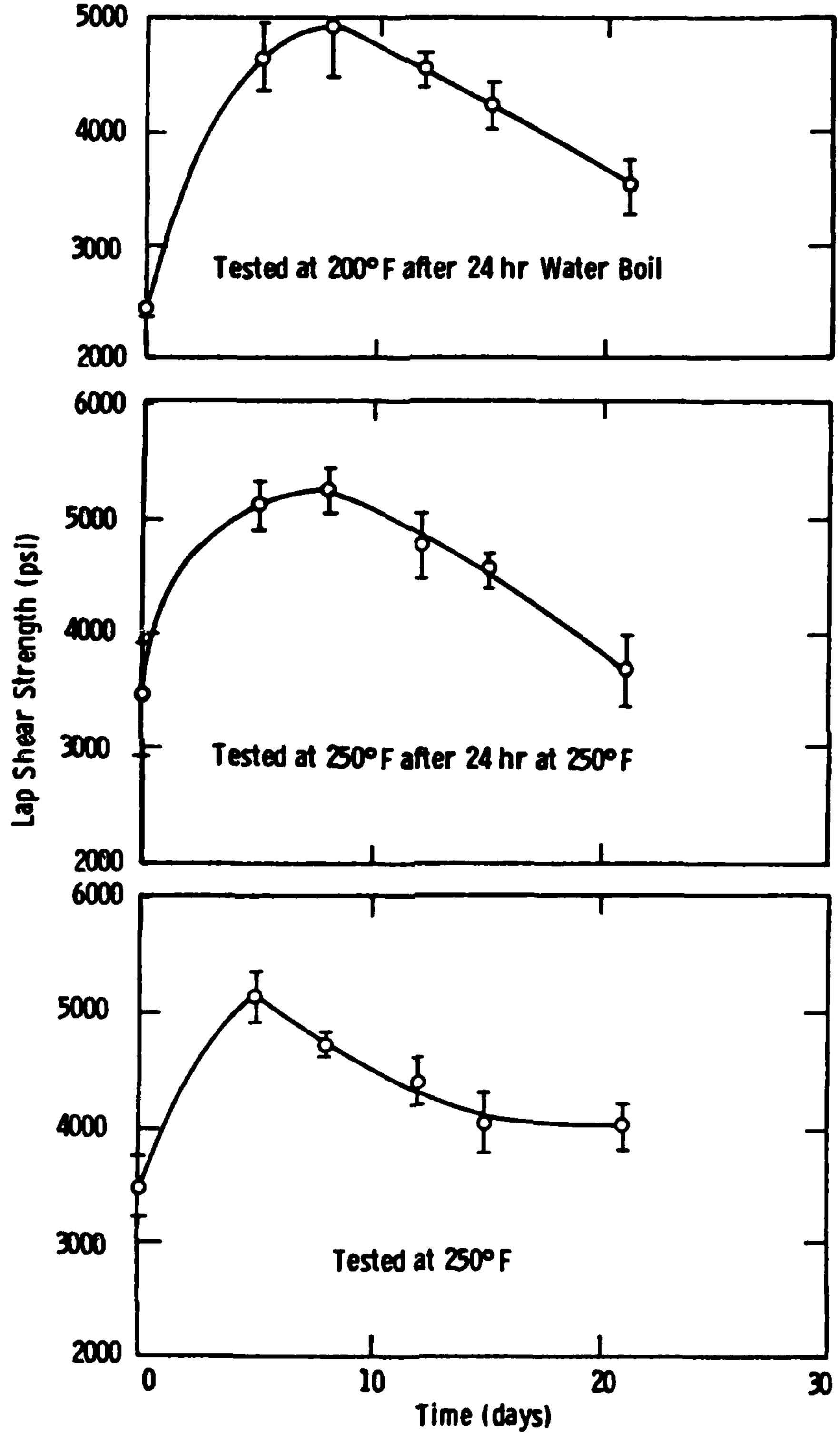


Fig. 4— Aging at 120°F, 20% R.H. Lap shear strength data for FM 300 adhesive (Lot B-360)

Curve 727644-B

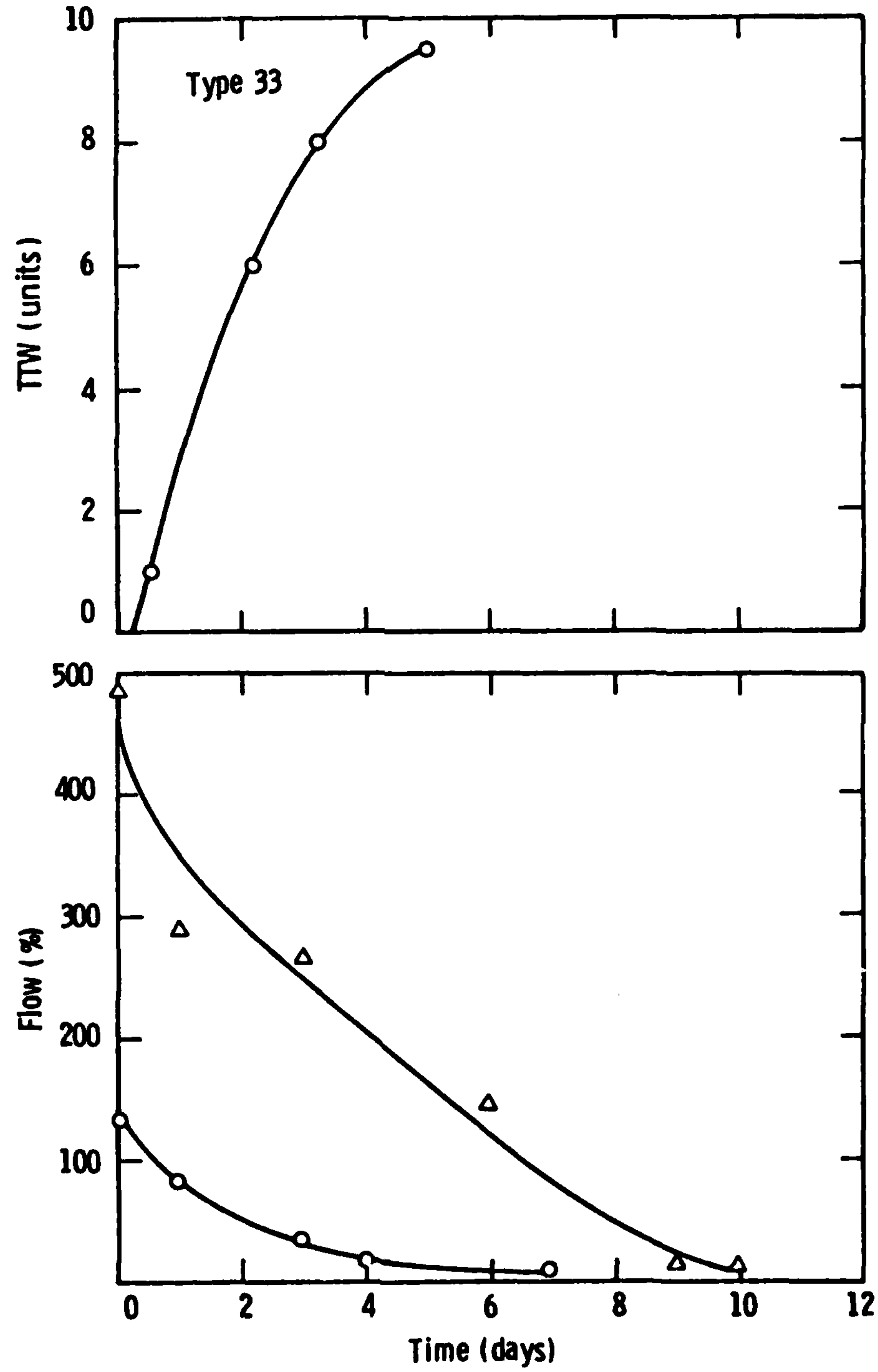


Fig. 5 — Aging at 120°F with 80% R.H., TTW and Flow data for FM 300 adhesive (-o- Lot B-377, -Δ- Lot B-360)

Curve 727646-B

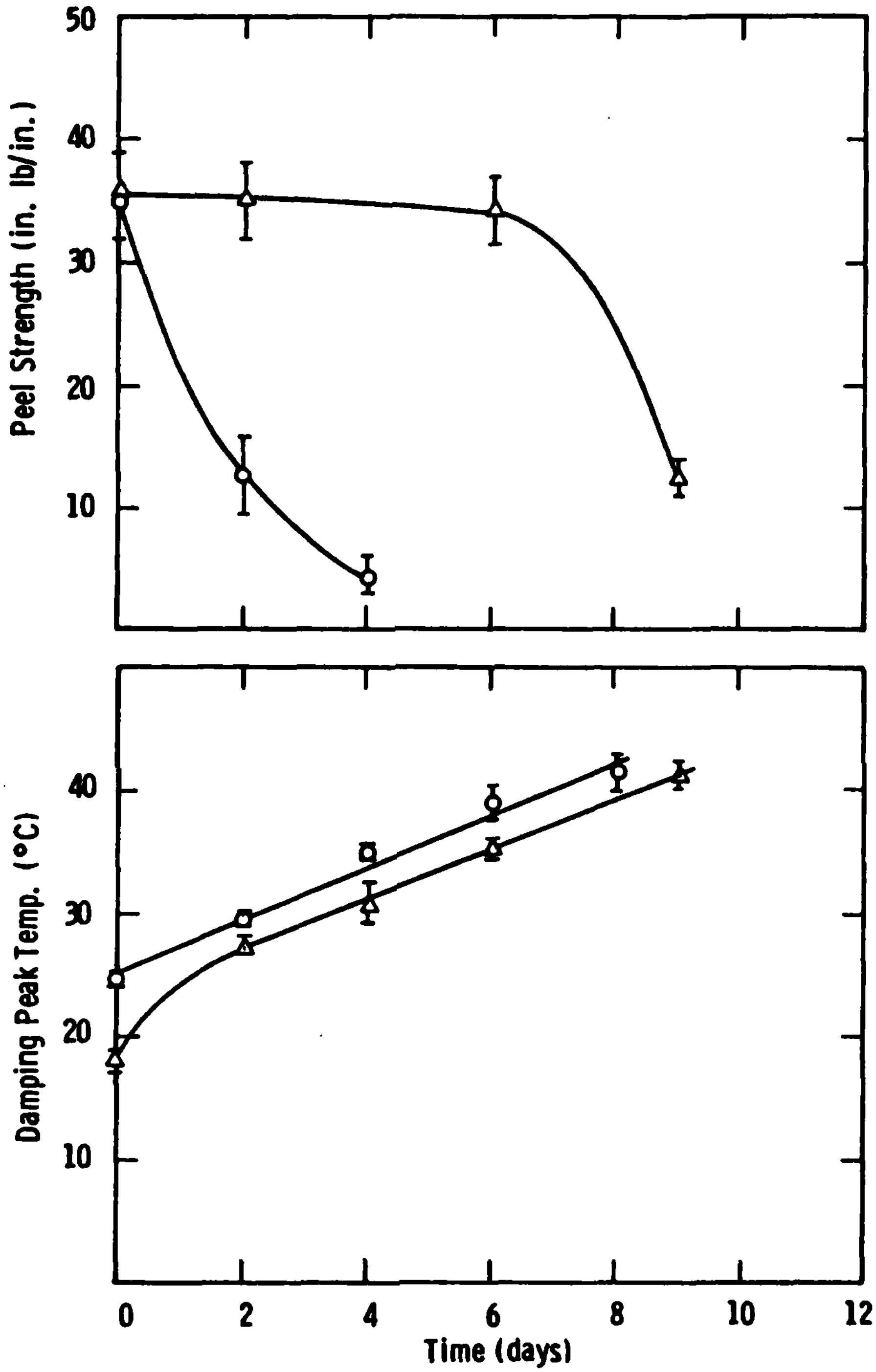


Fig. 6 — Aging at 120°F with 80% R.H. DMA and climbing drum peel strength data for FM 300 adhesive (-○- Lot B-377, -△- Lot B-360)

Curve 727641-A

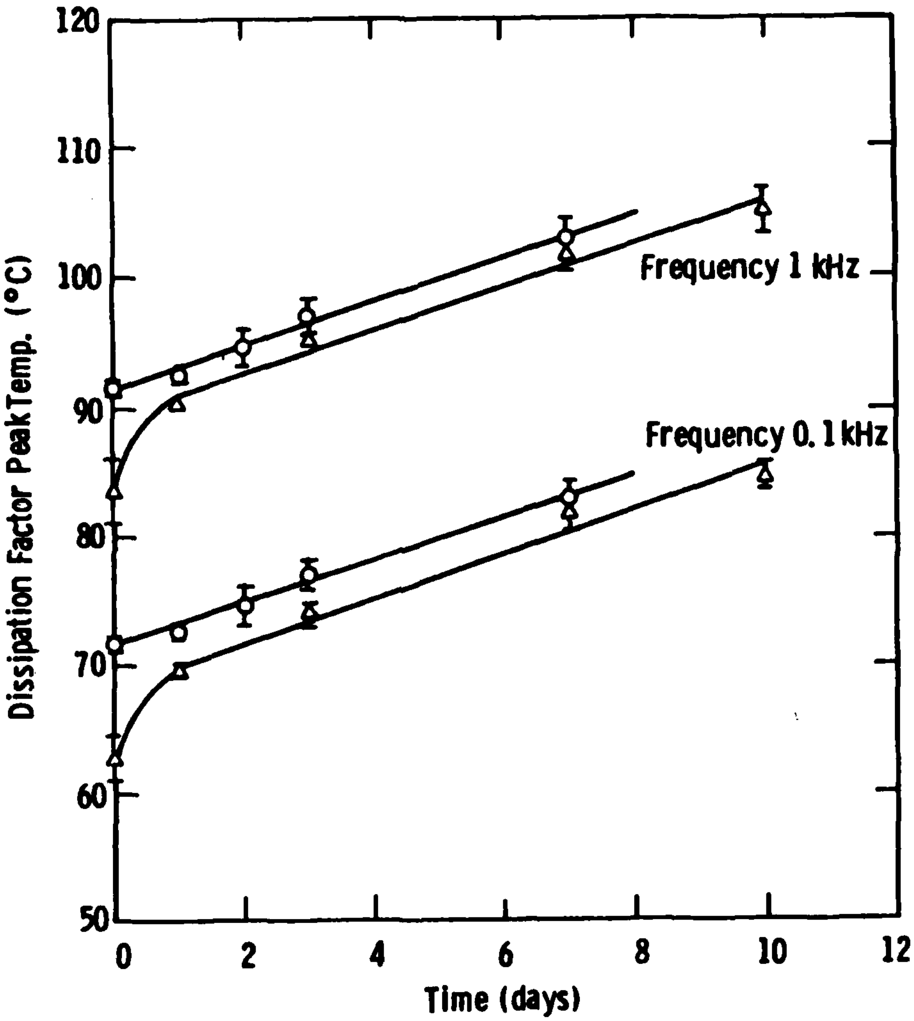


Fig. 7 — Aging at 120° F with 80% R.H. Dielectric analysis data for FM 300 adhesive. (-○- Lot B-377, △ Lot B-360)

Curve 727642-A

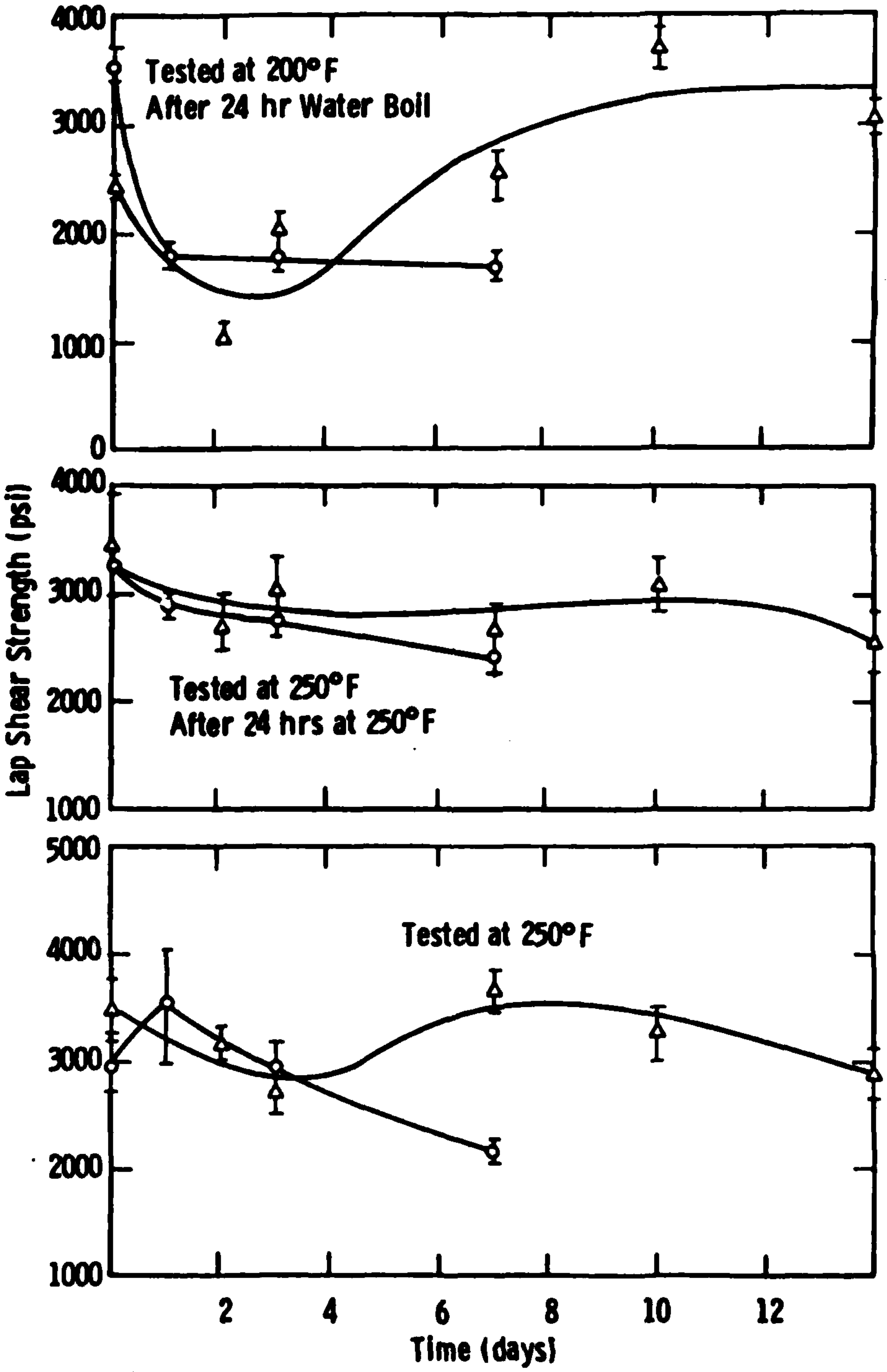


Fig. 8 — Aging at 120°F with 80% R.H. Lap shear strength data for FM 300 adhesive (-o- Lot B-377, -Δ- Lot B-360)

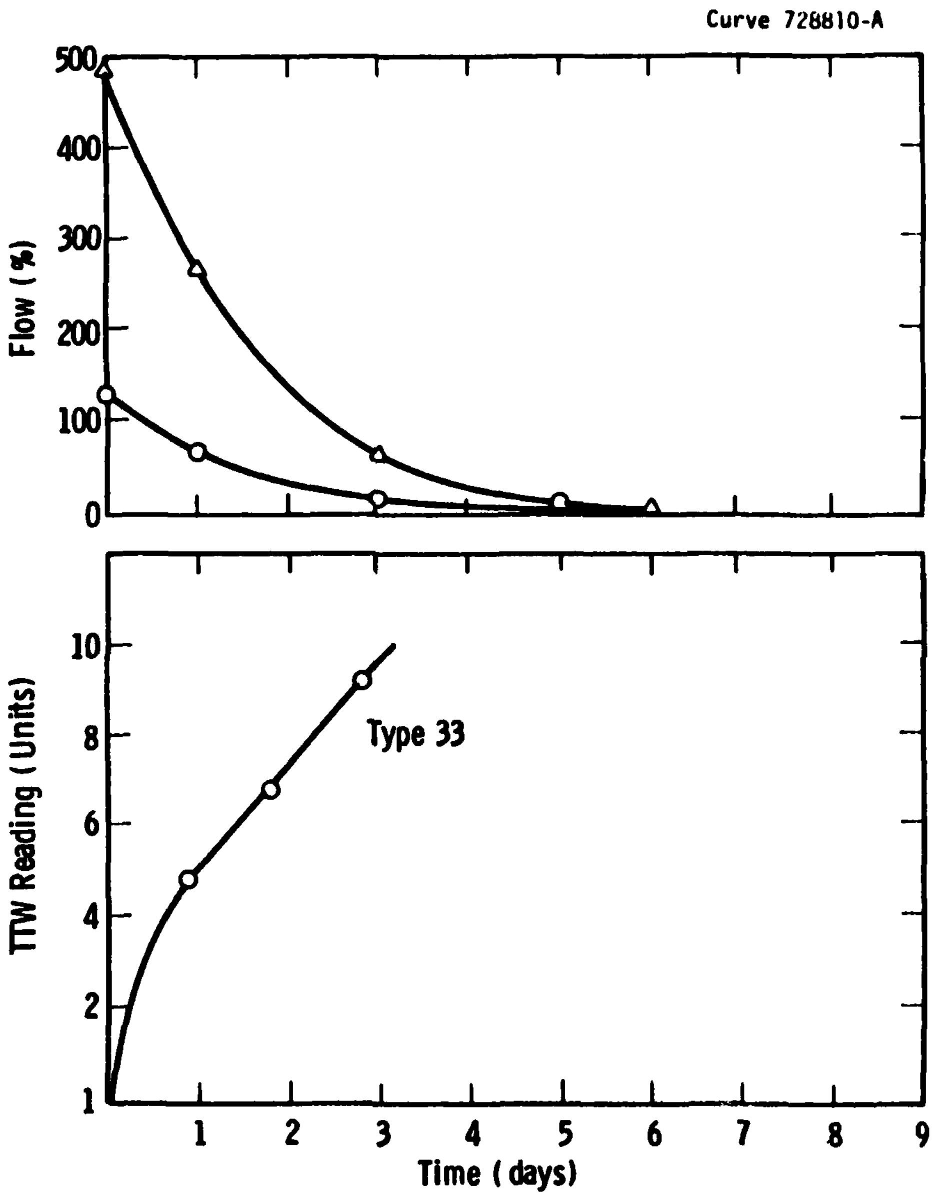


Fig. 9—Aging at 140°F and 80% R.H. Flow and TTW data for FM 300 adhesive (o-Lot B-377, △-Lot B-360)

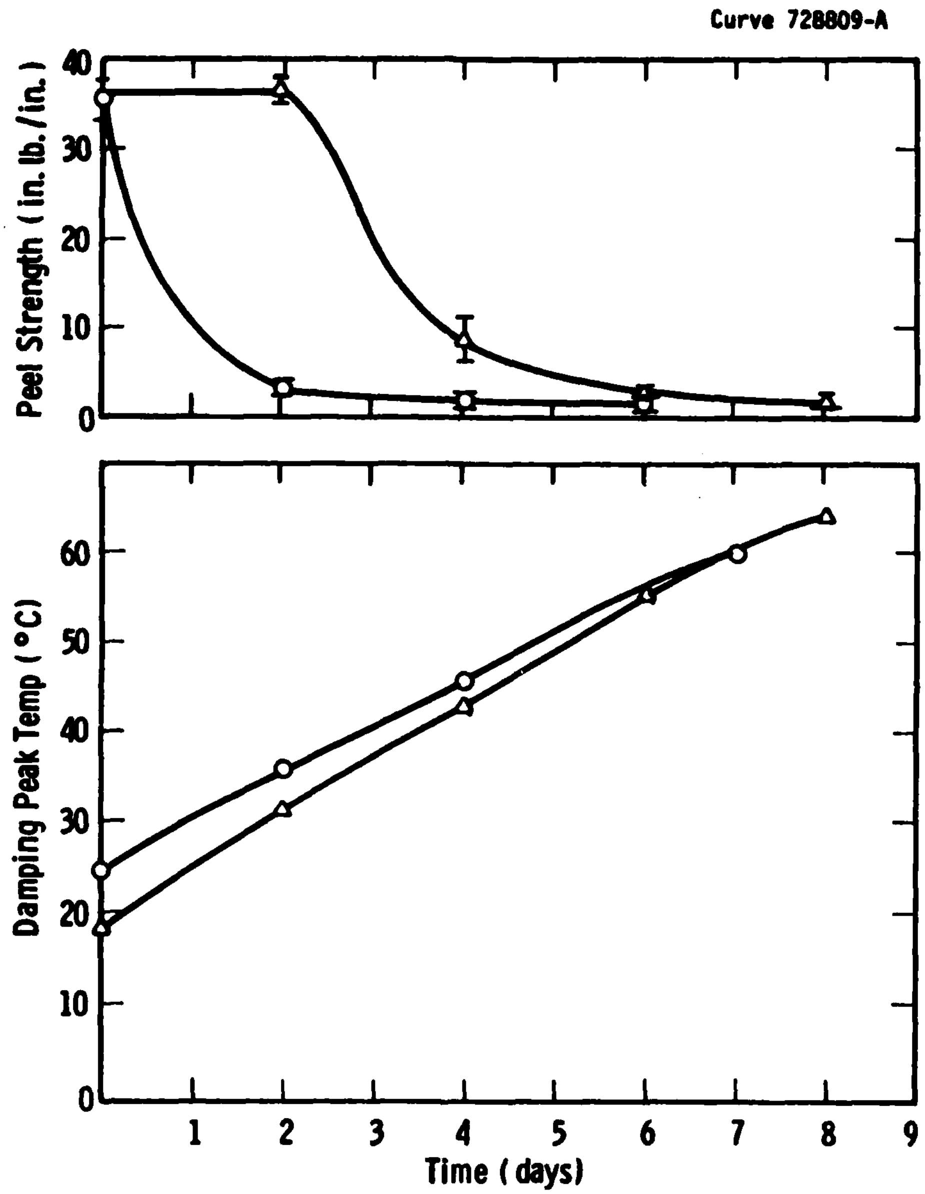


Fig. 10 —Aging at 140°F and 80 % R. H. Climbing drum peel strength and DMA data for FM300 adhesive. (○ -Lot B-377, △ -Lot B-360)

Curve 729718-A

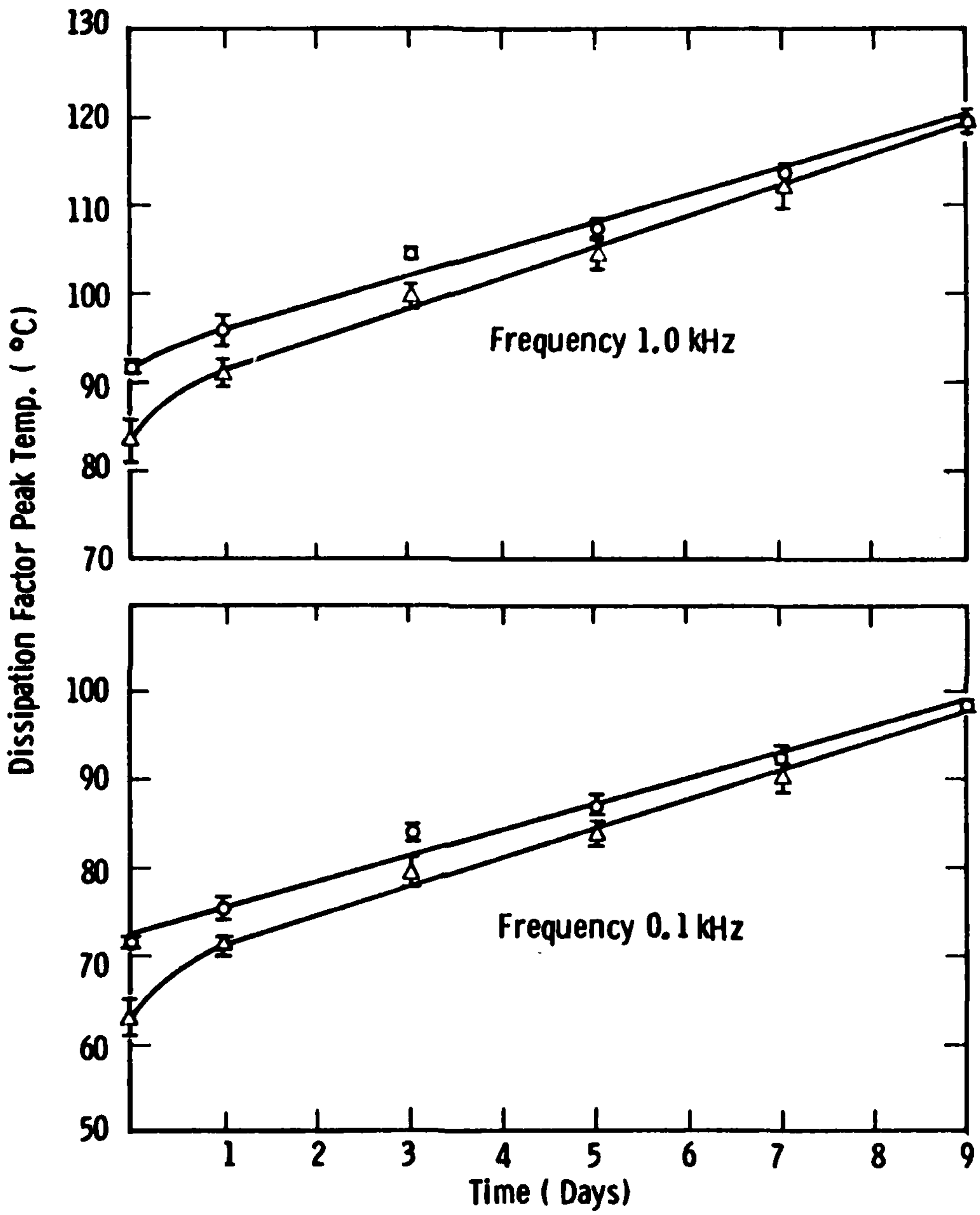


Fig. 11 – Aging at 140°F and 80 % R.H. Dielectric analysis data for FM300 adhesive. (o Lot B-377, △ Lot B-360)

Curve 728811-A

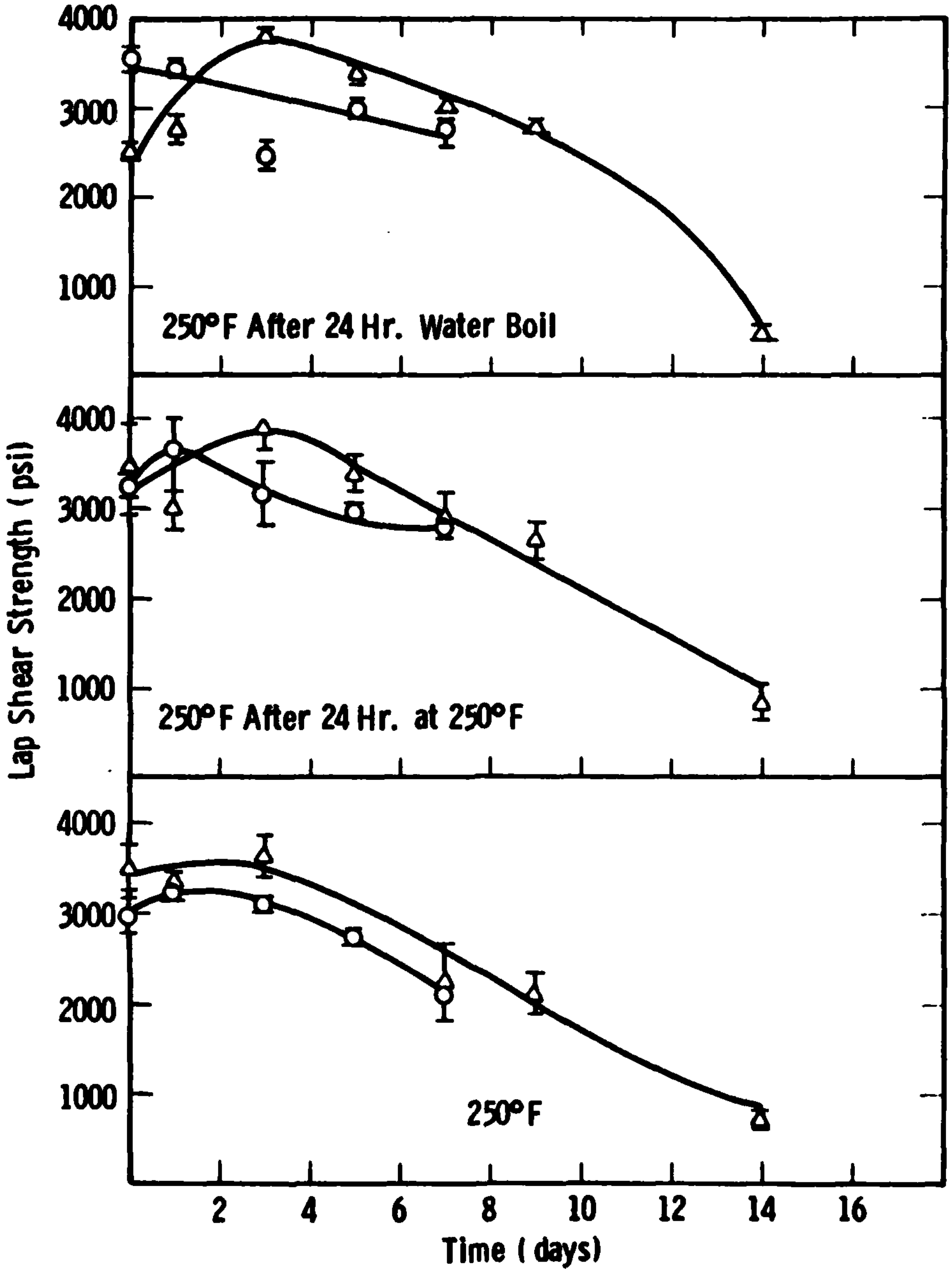


Fig. 12—Aging at 140°F and 80% R.H. Lap shear strength data for FM 300 adhesive (○ - Lot B-377, △ - Lot B-360)

Curve 731240-A

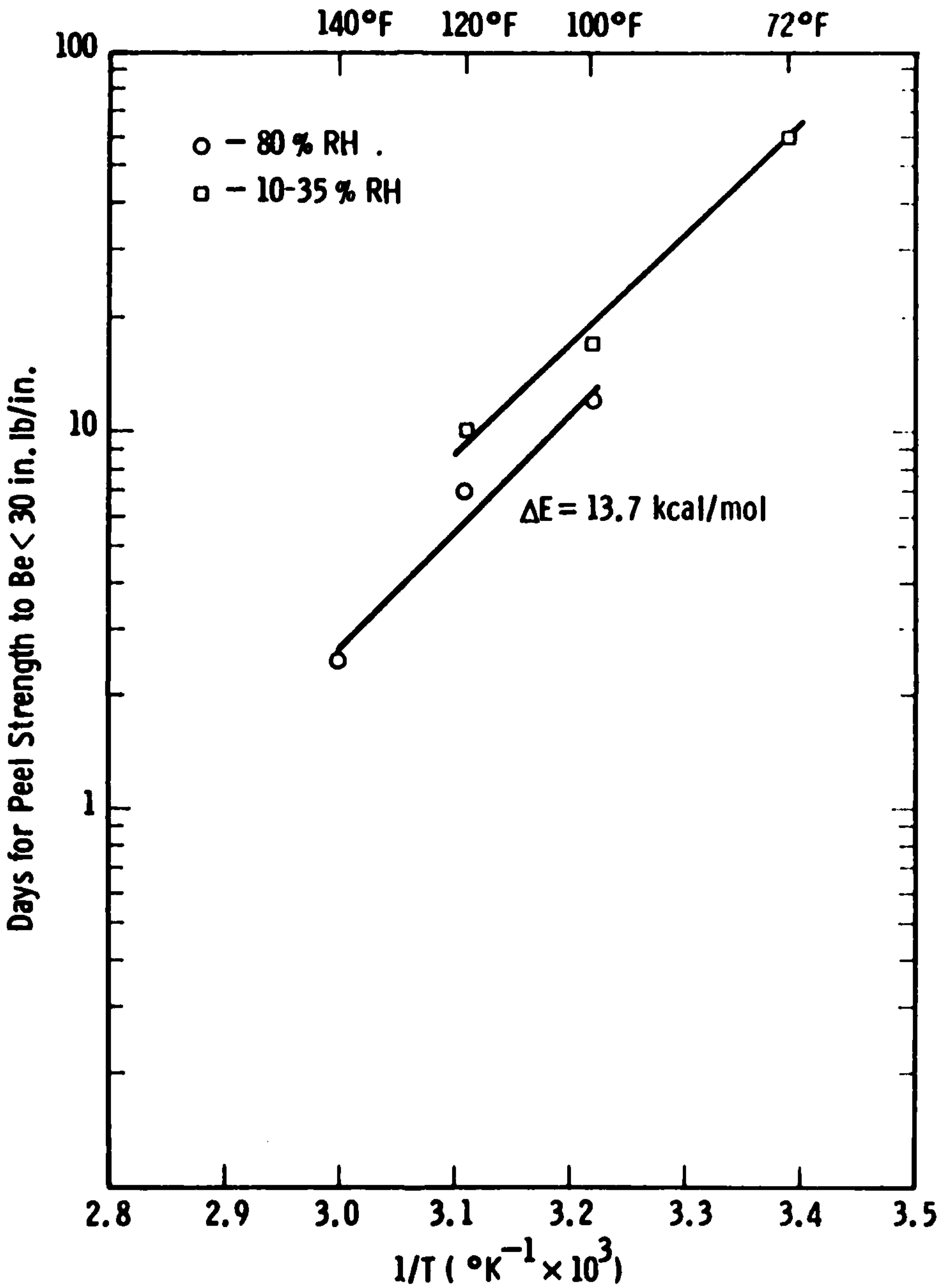


Fig. 13— FM300 End of storage life

DISTRIBUTION LIST FOR REPORTS UNDER N00019-80-C-0596

	Copies
Commander Naval Air Systems Command Department of the Navy Washington, D. C. 20361 ATTN: Code AIR-5304	8
Commander Naval Air Systems Command Department of the Navy Washington, D. C. 20361 ATTN: Code AIR-954	12
Commander Naval Air Systems Command Department of the Navy Washington, D. C. 20361 ATTN: Code AIR-320A	1
Commander Naval Surface Weapons Center White Oak Silver Spring, MD 20910 ATTN: Dr. Joseph Augl (234)	1
Air Force Materials Laboratory Wright-Patterson Air Force Base Ohio 45433 ATTN: Codes MBC LAM LN MXE LT MLBC	6
Director Plastics Technical Evaluation Center Picatinny Arsenal Dover, NJ 07801	2
Hercules Incorporated Magna, Utah 84044 ATTN: Mr. E. G. Crossland	1
TRW One Space Park Rodundo Beach, CA 90278 ATTN: R. W. Vaughan	1

DISTRIBUTION LIST FOR REPORTS UNDER N00019-80-C-0596 (Cont'd)

	Copies
University of Maryland College Park, MD 20742 ATTN: Dr. W. J. Bailey	1
Naval Research Laboratory Washington, D. C. 20375 ATTN: Dr. W. D. Bascom, Chemistry Division (Code 6170)	1
North American Aviation Rockwell International - Columbus Division 4300 E. Fifth Avenue Columbus, OH 43216	1
Commanding Officer Naval Air Development Center Warminster, PA 18974 ATTN: Aero Materials Laboratory (Structures Division)	1
Northrop Corporation 1001 E. Broadway Hawthorne, CA 90250 ATTN: Technical Library	1
Lockheed California Co. Dept. 74-54, Bldg 63 Box 551 Burbank, CA 91503 ATTN: Mr. J. H. Wooley	1
Naval Research Laboratory Washington, D. C. 20350 ATTN: Code 6120 (1 copy) Code 8433 (1 copy)	2
The Boeing Company Aerospace Division P. O. Box 3707 Seattle, WA 98124 ATTN: Library	1
Office of Naval Research Washington, D. C. 20361 ATTN: Code 472	1
NASA Headquarters 600 Independence Ave., S. W. Washington, D. C. 20546 ATTN: Mr. Charles F. Bersch	1

DISTRIBUTION LIST FOR REPORTS UNDER N00019-80-C-0596 (Cont'd)

	Copies
Battelle Columbus Laboratories 505 King Avenue Columbus, OH 43201	1
Commander Naval Material Command Headquarters Washington, D. C. 20360 ATTN: Code MAT 04H	1
Lockheed Missiles and Space Center Sunnyvale, CA 94088 ATTN: Mr. Clayton May	1
Materials Engineering Laboratory Picatinny Arsenal Dover, NJ 07801 ATTN: Mr. R. F. Wegman	1
National Academy of Science 2101 Constitution Ave., N. W. Washington, D. C. 20418 ATTN: Dr. R. S. Shane, NMAB	1
McDonnell-Douglas Corporation P. O. Box 516 St. Louis, MO 63166 ATTN: Dr. James Carpenter	1
McDonnell-Douglas Corporation P. O. Box 516 St. Louis, MO 63166 ATTN: Mr. Ray Juergens	1
American Cyanamid Co. Bloomingdale Dept. Havre de Grace, MD 21078 ATTN: Mr. R. B. Krieger	1

END

FILMED

1-83

DTIC